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(21) International Application Number: PCT/EP97/00118 (22) International Filing Date: 6 January 1997 (06.01.97) (30) Priority Data: 9601920.3 31 January 1996 (31.01.96) GB (71) Applicant (for AU BB CA GB IE IL KE LC LK LS MG MW NZ SD SG SZ TT UG only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA GB IE IL KE LC LK LS MG MW NZ SD SG SZ TT UG): UNILEVER N.V. (NL/NL); Weena 455, NL-3013 AL Rotterdam (NL). (72) Inventors: CRISOLOGO, Reiner, Jumao-as; Abdul Wahab Al-Ghamdi Building, Ground floor, Flat 3, Zaynal St. Ghulayl District, Al Mahjar Road, Jeddah (SA). GAR-CIA, Marcelito, Abad; Abdul Wahab Al-Ghamdi Building, Ground floor, Flat 3, Zaynal St. Ghulayl District, Al Mahjar Road, Jeddah (SA). JORDAN, David, Alan; 22 Alcazar, Sierra Village, Arabian Homes, Jeddah (SA). (74) Agent: MOLE, Peter, Geoffrey; Unilever PLC, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PROCESS FOR THE PRODUCTION OF A DETERGENT COMPOSITION		
(57) Abstract A process for the production of a low to medium bulk density detergent composition by mixing a liquid binder and a particulate starting material in a high speed mixer/granulator to form granules which are then contacted with a particulate material having a bulk density of not more than 700g/l in very low shear mixing zone for example a fluid bed. Compositions produced by this process are also disclosed.		

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PROCESS FOR THE PRODUCTION OF A DETERGENT COMPOSITION

The present invention relates to a process for the production of a detergent composition. In particular the invention is concerned with a process for the production of a detergent composition having a medium bulk density without the use of a spray-drying step involving a high shear mixing step and a very low shear mixing step and to detergent compositions thereby produced.

Conventionally, detergent compositions have been produced by a spray-drying process in which the components of the composition are mixed with water to form an aqueous crutcher slurry which is then sprayed into a spray-drying tower and contacted with hot air to remove water whereby detergent particles, often referred to as a "base" powder are obtained. The particles so obtained, have a high porosity. Thus powders produced by this method typically have a bulk density of 300 to 550 g/l or even up to 650 g/l.

Spray-dried powders generally provide good powder delivery characteristics such as dispensing and dissolution. However, the capital and operating costs of the spray-drying process are high. Nevertheless there remains a significant consumer demand for such low density powders.

In recent years, detergent powders having a high bulk density have been produced by mechanical mixing processes. Bulk densities of 700 to 900 g/l and even higher have been obtained. Typically such powders are produced by densifying a spray-dried base powder in one or more mechanical mixers, optionally with the addition of further components, or by mixing the components of the composition in a continuous or batch mixing process without the use of a spray-drying step.

EP 367 339 (Unilever) discloses a process for the production of a detergent composition having a high bulk density in which a particulate starting material is treated in a high speed mixer, a moderate speed mixer wherein the material is brought into or maintained in a deformable state, and then dried and/or cooled. The starting material may be a spray-dried base powder or the components of the composition may be employed without a prior spray-drying step in the detergent production process.

Powders having a high bulk density have a low packing volume which is advantageous for storage and distribution operations and also for the consumer. Furthermore, if a spray-drying step is not employed, the capital and operating costs are typically much lower and the process uses less energy and so provides an environmental benefit. The avoidance of a spray-drying step in the detergent production process is therefore desirable.

However, such high density powders typically have a much lower porosity than a conventional spray-dried powder which may impair the delivery of the powder into the wash liquor. Additionally, the production of powders having a low to medium bulk density, for example less than about 700 g/l, has not hitherto been readily achievable on a commercial scale without the use of a spray-drying step.

EP 544 365 (Unilever) is concerned with the production of a high bulk density detergent composition and refers to the bulk density of a detergent powder being dependent upon the bulk density of the starting materials in the case of a mixing process.

Treating a porous spray-dried material in a mechanical mixing process typically leads to an increase in bulk density

as the powder porosity is reduced. However, we have found that a powder having a surprisingly low bulk density, for example less than 700 g/l, may be obtained by a process in which a spray-drying step is not employed, involving a high shear mixing step and a very low shear mixing step if a component having a low bulk density is incorporated in the very low shear mixing step. Further, such a powder exhibits good powder properties.

A first aspect of the invention provides a process for the production of a detergent composition or component having a bulk density of less than 700 g/l which does not comprise a spray-drying step and which process comprises mixing a particulate starting material with a liquid binder in a mixer granulator, preferably having both a stirring and a cutting action, to form granules wherein the starting material and/or binder comprises a non-soap detergent active or a precursor thereof, feeding the said granules to a very low shear mixing zone and contacting the granules with a particulate material having a bulk density of not more than 700g/l to produce a detergent composition or component having a bulk density of less than 700 g/l.

A second aspect of the invention provides a detergent composition or component having a bulk density of less than 700 g/l obtainable by a process which does not comprise a spray-drying step and which comprises mixing a particulate starting material with a liquid binder in a mixer/granulator, preferably having both a stirring and cutting action, to form granules and feeding the said granules to a very low shear mixing zone and contacting the granules with a particulate material having a bulk density of not more than 700g/l.

Unless stated otherwise, % figures are on a weight basis and based on the total weight of the detergent composition or

component prior to the optional addition of post-dosed ingredients.

Suitably the detergent composition has a bulk density of 400 to 680 g/l, preferably 450 to 680 g/l and more preferably 500 to less than 650 g/l. It is further preferred that the detergent composition has a particle porosity of at least 0.2 and more preferably at least 0.25. The porosity may be determined by a mercury porosimetry method.

The component incorporated in the very low shear zone has a bulk density of not more than 700 g/l, and suitably has a bulk density of 200 to 600 g/l, preferably 250 to 550 g/l and especially 350 to 500 g/l.

This low bulk density component is desirably an aluminosilicate, for example zeolite 4A or zeolite A24 or a salt, preferably an inorganic salt. Salts, preferably sodium, of phosphates, for example tripolyphosphate, carbonate, bicarbonate and sulphate are especially suitable. Desirably the low bulk density component constitutes the detergency builder, or part thereof in the composition. If desired, this component may be a non-builder material, in which case the particulate starting material will suitably comprise a builder.

It is especially preferred that the low bulk density component comprises sodium tripolyphosphate having a bulk density of 380 to 500 g/l. This compares to a typical bulk density of 800 to 1000 g/l for tripolyphosphate conventionally employed in detergent compositions.

Suitably the level of the low bulk density component is selected according to the desired density of the detergent composition. Preferably it is present at a level of 5 to

65 wt %, preferably 10 to 40 wt % and optimally 10 to 30 wt % of the composition.

If desired part of the low bulk density component may be introduced into the high speed mixer/granulator. In a preferred embodiment, the level of this component in the very low shear mixing zone is at least 10% by weight based on the detergent composition and additionally up to 80% of the total amount of the low bulk density component may be dosed into the high speed mixer/granulator although it is preferred that up to 60%, more preferably 5 to 50%, especially 20 to 45% of the low density material (as a percentage of the total amount of this material) be dosed into the high speed mixer granulator.

The process may be continuous but is preferably batch-wise.

A preferred type of mixer/granulator for use in the process of the invention is bowl-shaped and preferably has a substantially vertical stirrer axis. Especially preferred are mixers of the Fukae (Trade Mark) FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another, and at separately variable speeds.

Other similar mixers found to be suitable for use in the process of the invention are the Diosna (Trade Mark) V series ex Dierks & Söhne, Germany; and the Pharma Matrix (Trade Mark) ex T K Fielder Ltd., England. Other similar mixers believed to be suitable for use in the process of the

invention include the Fuji (Trade Mark) VG-C series ex Fuji Sangyo Co., Japan; and the Roto (Trade Mark) ex Zanchetta & Co srl, Italy.

5 Another mixer found to be suitable for use in the process of the invention is the Lödige (Trade Mark) FM series batch mixer ex Morton Machine Co. Ltd., Scotland. This differs from the mixers mentioned above in that its stirrer has a horizontal axis.

10 Granulation is preferably effected by running the mixer using both stirrer and cutter; a relatively short residence time (for example, 5-8 minutes for a 35 kg batch) is generally sufficient. The final bulk density can be
15 controlled by choice of residence time.

 Suitably the stirrer is operated at a rate of 25 to 80 rpm, preferably 30 to 75 rpm. Independently the cutter is
20 suitably operated at a rate of 200 to 2500 rpm, preferably 300 to 2200 rpm. A batch process typically involves pre-mixing of solid components, addition of liquids, granulation, optional addition of a layering material suitable for
 controlling the granulation end-point, and product discharge. The rate of stirring and/or cutting is suitably adjusted
25 according to the stage of the process.

 The presence of a liquid binder is necessary for successful granulation. The precise nature of the binder is not critical provided that it enables successful granulation
30 to be achieved. Suitably the binder comprises one or more of the following: liquid detergent-active compound(s), precursors thereof, water, solutions, non-aqueous or aqueous, of other ingredients or mixtures thereof. If water is employed the level is desirably controlled so that the

moisture content of the detergent composition is not more than 10% by weight and preferably not more than 6%.

The mixing step is preferably carried out at a controlled temperature somewhat above ambient, preferably above 30°C. Suitably the temperature is within the range 30 to 55°C although higher temperatures may be suitable, for example, where heat of reaction is generated by in situ neutralisation.

The very low shear mixing zone may be located within the same apparatus as the high speed mixer granulation but desirably is in a separate apparatus for example a rotating bowl mixer and preferably a fluid bed. The fluid bed is suitably operated at a temperature of 30 to 90°C and at a superficial air velocity of about 0.25 to 1.2 ms⁻¹. Suitable fluid beds are available from, for example NIRO. The air flow in the fluid bed may be adjusted according to the desired level of shear and agitation of the low bulk density component. Suitably the low bulk density component is dosed into the bed and gently agitated using a small air flow which is then increased prior to feeding in the granules from the high speed mixer/granulator.

The detergent composition suitably comprises anionic detergent active. This may be incorporated as a pre-neutralised material, desirably as a component of the particulate starting material, or may be neutralised in situ. In the latter case the acid precursor of the active is preferably neutralised using a solid neutralising agent, for example carbonate (preferably sodium carbonate), which is desirably a component of the particulate starting material.

The detergent active material present in the composition may be selected from anionic, ampholytic, zwitterionic or

nonionic detergent active materials or mixtures thereof. Examples of suitable synthetic anionic detergent compounds are sodium and potassium (C_9 - C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10} - C_{15}) benzene sulphonates; sodium or potassium alkyl sulphates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. Suitable nonionics which may be employed include, in particular the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6 - C_{22}) phenol ethylene oxide condensates, generally having 5 to 25 EO, ie 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic (C_6 - C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO. The level of detergent active material present in the composition may be in the range from 1 to 50% by weight depending on the desired applications. Nonionic material may be present in the particulate starting material at a level which is preferably less than 10% by weight, more preferably less than 5% by weight and/or employed as the liquid binder optionally with another liquid component, for example water.

In a preferred embodiment of the invention, the particulate starting material comprises one or more of a carbonate salt at a level of 5 to 60 wt %, a zeolite at a level of 5 to 60 wt % and, if present as the low bulk density component, a phosphate salt at a level of 5 to 20% by weight of the total quantity of starting material.

Suitably the particulate starting material constitutes 30 to 70% of the detergent composition.

5 Optionally, a layering material may be employed during the high speed mixing step to control granule formation and reduce or prevent over-agglomeration. Preferably a layering material is introduced into the very low shear mixing step. Suitable materials include aluminosilicates, for example zeolite 4A and A24. The layering material is suitably
10 present at a level of 1 to 4 wt % based on the composition.

 The composition may be used as a complete composition in its own right or may be mixed with other components or mixtures and thus may form a major or minor part of a final
15 product. The composition may be blended with for example a spray-dried base powder.

 Conventional additional components such as enzymes, bleach and perfume may also be admixed with the composition
20 as desired to produce a fully formulated product.

 The invention is further illustrated by the following non-limiting Examples.

Example 1 and A (Comparative)

5 A detergent composition was prepared by dosing the following components into a Fukae FS3500 mixer (in the following sequence):

Sodium Tripolyphosphate (400-440g/l)	80 (kg)
Fluorescer	1
SCMC	12
Sodium Carbonate	530
LAS acid	170
Fatty acid (PRISTERENE 4918)/Nonionic mixture	40/30

15 The process conditions employed are summarised below:

<u>Process step</u>	<u>Stirrer (rpm)</u>	<u>Cutter (rpm)</u>
Solids premix	40	0
20 Liquids addition	75	1900
Granulation	70	1900
Discharge	30-45	1500

25 The mixer was operated at a temperature of 30-35°C. The mixer was operated for sufficient time to effect granulation in the granulation step (end point 60 amps) and the product was discharged over 240 seconds.

30 130kg of sodium tripolyphosphate (bd 400-440g/l) was dosed into a NIRO fluid bed and 'bubbled' at a low air velocity. Prior to discharge of the granules from the Fukae mixer, the air flow was increased to about 11000 m³/hr and the granules were fed into the fluid bed.

20kg of zeolite 4A was then dosed into the fluid bed as a layering material. The detergent composition was then discharged from the fluid bed at a temperature below 30°C.

For comparative purposes the above procedure was repeated to produce Composition A, but conventional density STP (about 800g/l) was substituted for the low density STP. All of the STP was dosed into the Fukae mixer and none into the fluid bed.

The properties of the two powders were measured and the results are detailed below:

	<u>Example 1</u>	<u>Comparative A</u>
Bulk density (g/l)	520	775
Dynamic		
Flow Rate (ml/s)	>90	>90
Mean particle size (µm)	520	750

Both powders were crisp and free flowing and white/cream in colour.

The results demonstrate that a medium bulk density powder is obtainable without the need for a spray-drying step in the production process. A reduction in bulk density may be expected to have an adverse effect on powder properties (compression, UCT). However these properties remain at an acceptable level for the powder of Example 1.

Claims

1. A process for the production of a detergent composition or component having a bulk density of less than 700 g/l which
5 does not comprise a spray-drying step and which process comprises mixing a particulate starting material with a liquid binder in a mixer granulator to form granules wherein the starting material and/or binder comprises a non-soap detergent active or a precursor thereof feeding the said
10 granules to a very low shear mixing zone and contacting the granules with a particulate material having a bulk density of not more than 700g/l to produce a detergent composition or component having a bulk density of less than 700 g/l.
- 15 2. A process according to claim 1, wherein the particulate material having a low bulk density comprises alumino-silicate, an inorganic salt or mixtures thereof.
- 20 3. A process according to claim 2, wherein low bulk density particulate material comprises a phosphate, carbonate, bicarbonate or sulphate salt.
- 25 4. A process according to any preceding claim, wherein the particulate material having low bulk density comprises a builder material.
- 30 5. A process according to any preceding claim, wherein 5-65% by weight of the low bulk density particulate material based on the composition is added.
- 35 6. A process according to any preceding claim, wherein at least 10% by weight based on the detergent composition of low bulk density particulate material is added in the very low shear mixing zone.

7. A process according to any preceding claim, wherein the binder comprises liquid detergent-active, liquid detergent-active precursor, water, solutions, non-aqueous or aqueous, of other ingredients, or mixtures thereof.

8. A process according to any preceding claim, wherein the active comprises anionic detergent active.

9. A process according to claim 8, wherein acid precursor of anionic detergent is added and neutralised in situ.

10. A process according to any preceding claim, wherein the particulate starting material comprises one or more of a carbonate salt at a level of 5-60 wt%, a zeolite at a level of 5-60 wt% and if present as the low bulk density component, a phosphate salt at a level of 5-20% by weight of the total quantity of starting material.

11. A detergent composition or component having a bulk density of less than 700 g/l obtainable by a process which does not comprise a spray-drying step and which comprises mixing a particulate starting material with a liquid binder in a mixer/granulator to form granules and feeding the said granules to a very low shear mixing zone and contacting the granules with a particulate material having a bulk density of not more than 700g/l.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/06 C11D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8523 Derwent Publications Ltd., London, GB; Class 025, AM 85-137896 XP002032014 & JP 60 072 998 A (KAO CORP) , 25 April 1985 see abstract ---	1,3,4, 7-9,11
A	WO 95 01418 A (UNILEVER) 12 January 1995 see claims --- -/-	1-5,7,11

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	<p>DATABASE WPI Section Ch, Week 9612 Derwent Publications Ltd., London, GB; Class D25, AN 96-112966 XP002032015 & JP 08 013 000 A (LION CORP) , 16 January 1996 see abstract</p> <p>---</p>	1-5,11
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Information on patent family members

International Application No.

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